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(71) Applicant *(for all designated States except US)*: ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: FISHER, Karl, J. [US/US]; 1116 South McDonald, Petaluma, CA 94954 (US). WOOLARD, Frank, X. [US/US]; 20 Corte Ramon, Greenbrae, CA 94904 (US). LEADBETTER, Michael, R. [US/US]; 335 Beverly Avenue, San Leandro, CA 94577 (US). GERDES, John, M. [US/US]; North 11922 Wood Road, Reardan, WA 99029 (US).

(74) Agents: THOMSON, Marian, T. et al.; Zeneca Inc., 1200 South 47th Street, Richmond, CA 94804 (US).

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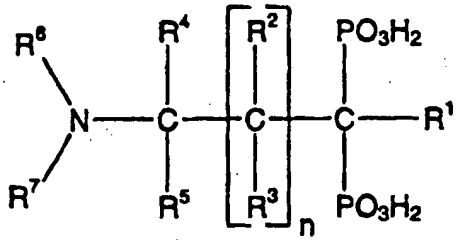
(54) Title: HERBICIDAL AZA BISPHOSPHONIC ACIDS AND COMPOSITIONS CONTAINING THE SAME

(57) Abstract

Herbicidal compositions containing a bisphosphonic acid compound of formula (I) wherein n is 1, 2, 3, 4, 5 or 6, or an agrochemically acceptable salt or hydrolyzable ester thereof and methods of controlling undesirable plant growth using these bisphosphonic acid containing compositions. The herbicidal compositions exhibit desirable efficacy when applied to plants post-emergence, but exhibit little significant activity when applied to plants pre-emergence. Novel aza-bisphosphonic acid compounds are also disclosed.



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HERBICIDAL AZA BISPHOSPHONIC ACIDS AND COMPOSITIONS CONTAINING THE SAME

FIELD OF THE INVENTION

This invention relates to herbicidal compositions containing an aza-bisphosphonic acid wherein the nitrogen atom and the carbon atom to which the two phosphonic acid groups are bound are linked by two to seven carbon atoms. In another aspect, this invention is directed to a method of controlling the undesirable growth of plants by applying to the area where control is desired an herbicidally effective amount of such an aza-bisphosphonic acid composition. In yet another aspect, this invention is directed to certain novel aza-bis-phosphonic acid compounds.

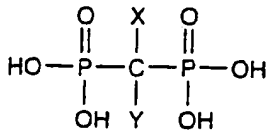
BACKGROUND OF THE INVENTION

The need for effective herbicides requires no special emphasis. The control of weeds and undesirable vegetation is of great economic importance since weed competition inhibits the production of foliage, fruit or seed of agricultural crops. The presence of weeds can reduce harvesting efficiency and the quality of the harvested crop. Weeds on noncropped areas may cause a fire hazard, undesirable drifting of sand or snow, and/or irritation to persons with allergies. Thus, suppression of undesirable weed growth is very advantageous.

Moreover, it is highly desirable to possess herbicides which exhibit desirable efficacy against plants when applied post emergently, but which further exhibit little significant activity when applied preemergently. Such herbicides will, for example, permit the control of weeds already present in a field but will not harm crops which have not yet emerged.

Accordingly, it is an object of this invention to provide effective novel herbicidal compositions and a novel method of controlling weeds, as well as certain novel herbicidal compounds. It is a further object of this invention to provide novel compositions, methods and herbicidal compounds which exhibit admirable postemergent control coupled with no significant preemergent control.

Japanese Patent Publication 54-147925 (Nissan Chemical) discloses herbicidal bisphosphonic acid compounds wherein the phosphonic acid groups are bound to a single carbon atom. Such compounds are of the formula:



wherein X and Y are each hydrogen, halogen, alkyl or cycloalkyl; or salts thereof.

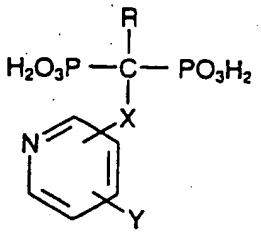
Herbicidal aza-bisphosphonic acid compounds wherein the carbon to which the two phosphonic acid groups are bound is directly linked to the nitrogen atom of the amino group are disclosed in U.S. Patent 4,447,256 (Suzuki et al.); British Patent 1,508,772 (Devlin); Japanese Patent Publication 54-37829 (Nissan Chemical); Japanese Patent Publication 54-144383 (Nissan Chemical); Japanese Patent Publication 55-98105 (Nissan Chemical); and in "Herbicide Properties of Aminophosphonic Acid Derivatives", Dr. Y. Okamoto, 1st International Congress on Phosphorus Compounds, Rabat, October 17-21, 1977, pp. 649-652.

The phytocidal properties of aminophosphonates structurally related to N-(phosphonomethyl)glycine, including a compound having the molecular formula:

$$[(HO)_2P(O)]_2C(NH_2)CH_2N(C_2H_5)_2,$$

are described in E. Bakuniak et al., "Further Studies on Biological Activity of Aminophosphonates Structurally Related to N-(Phosphonomethyl)glycine." Journal of Environmental Science and Health, Vol. B18, Nos. 4 and 5, pp. 485-496 (1983).

Japanese Patent Publication 55-98193 discloses certain herbicidal compounds of the formula



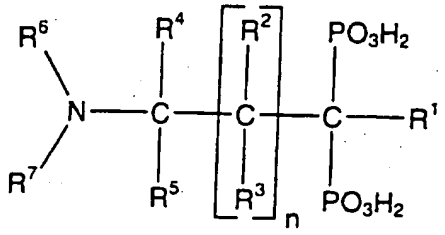
wherein R is H, lower alkyl or halogen; X is $-CH_2-$, S or O; Y is H, lower alkyl or halogen; and alkali salts thereof.

Although certain aza-bisphosphonic acid compounds wherein the carbon to which the two phosphonic acid groups are bound is linked to a nitrogen atom via one or more carbon atoms have been disclosed in the art, these particular compounds are not indicated to have herbicidal activity. Thus, U.S. Patent 3,962,318 discloses compounds useful as flame retardants, and German Patent DE 2754821 discloses compounds useful as chelators in water treatment. U.S. Patent 5,133,972, U.S. Patent 4,990,503, U.S. Patent 4,254,114, U.S. Patent 4,666,895, U.S. Patent 4,927,814, U.S. Patent 4,939,130, U.S. Patent 4,942,157, European Patent Publication 96,931, European Patent Publication 96,933, European Patent Publication 186,405, European Patent Publication 274,158, European Patent Publication 522,576, European Patent Publication 513,760, PCT Patent Publication WO 93/24500, German Patent Publication DE 3,804,686 and German Patent Publication DE 3,626,058 all disclose pharmaceutical uses for the specific compounds disclosed therein.

SUMMARY OF THE INVENTION

In one aspect, this invention is directed to an herbicidal composition comprising:

(A) an herbicidally effective amount of a compound of the Formula (I):



(I)

wherein n is 1, 2, 3, 4, 5 or 6;

R^1 is hydrogen, hydroxy, C_1-C_4 alkoxy, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, hydroxy-C_1-C_4-alkyl, hydroxy-C_1-C_4-alkoxy or $N(R^8)(R^9)$ wherein R^8 and R^9 are each independently hydrogen or C_1-C_3 alkyl;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{12})(R^{13})$ wherein R^{12} and R^{13} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^6 and R^7 together with the nitrogen to which they are bound form an aziridine; piperazine; morpholine; thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole; tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, halo, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10} alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^6 or R^2 and R^6 together with the nitrogen and carbon atoms to which they are bound form an aziridine; piperazine; morpholine, thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole, tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline; or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^2 and R^4 together with the carbon atoms to which they are bound form a C_5-C_6 cycloalkyl or cycloalkenyl ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10} alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

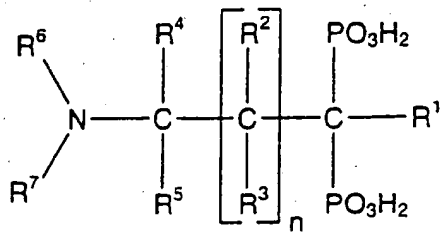
R^4 and R^5 together form a 3-6 membered carbocyclic ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio or $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are each independently hydrogen or C_1-C_{12} alkyl; and

m is 0, 1 or 2;

or an agrochemically acceptable salt or hydrolyzable ester thereof; and

(B) an agrochemically acceptable carrier therefor.

In another aspect this invention is directed to a method of controlling the growth of plants comprising applying to the locus of such plants an herbicidally effective amount of a compound of the Formula (I):



(I)

wherein n is 1, 2, 3, 4, 5 or 6;

R^1 is hydrogen, hydroxy, C_1-C_4 alkoxy, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, hydroxy-C_1-C_4-alkyl, hydroxy-C_1-C_4-alkoxy or $N(R^8)(R^9)$ wherein R^8 and R^9 are each independently hydrogen or C_1-C_3 alkyl;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{12})(R^{13})$ wherein R^{12} and R^{13} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^6 and R^7 together with the nitrogen to which they are bound form an aziridine; piperazine; morpholine; thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole; tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, halo, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^6 or R^2 and R^6 together with the nitrogen and carbon atoms to which they are bound form an aziridine; piperazine; morpholine, thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole;

imidazole; pyrrole; triazole, tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline; or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^2 and R^4 together with the carbon atoms to which they are bound form a C_5-C_6 cycloalkyl or cycloalkenyl ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}- alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^5 together form a 3-6 membered carbocyclic ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio or $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are each independently hydrogen or C_1-C_{12} alkyl; and

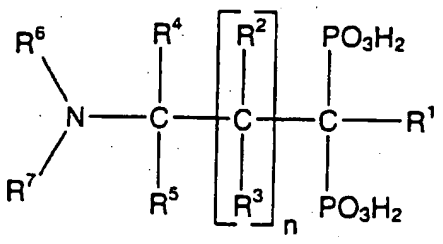
m is 0, 1 or 2;

or an agrochemically acceptable salt or hydrolyzable ester thereof.

In yet another aspect, this invention is directed to novel aza-bisphosphonic acid compounds having a structure within the scope of Formula (I) above.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compounds employed in the herbicidal compositions of this invention are of the Formula (I):



(I)

wherein n is 1, 2, 3, 4, 5 or 6;

R^1 is hydrogen, hydroxy, C_1-C_4 alkoxy, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, hydroxy-C_1-C_4-alkyl, hydroxy-C_1-C_4-alkoxy or $N(R^8)(R^9)$ wherein R^8 and R^9 are each independently hydrogen or C_1-C_3 alkyl;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{12})(R^{13})$ wherein R^{12} and R^{13} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^6 and R^7 together with the nitrogen to which they are bound form an aziridine; piperazine; morpholine; thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole; tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, halo, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^6 or R^2 and R^6 together with the nitrogen and carbon atoms to which they are bound form an aziridine; piperazine; morpholine, thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole, tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline; or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^2 and R^4 together with the carbon atoms to which they are bound form a C_5-C_6 cycloalkyl or cycloalkenyl ring; any of which may be optionally substituted with C_1-C_{12} alkyl,

hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}- alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^5 together form a 3-6 membered carbocyclic ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio or $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are each independently hydrogen or C_1-C_{12} alkyl; and

m is 0, 1 or 2;

or an agrochemically acceptable salt or hydrolyzable ester thereof.

Preferably:

R^1 is hydrogen, hydroxy, halogen or C_1-C_4 alkyl;

R^2, R^3, R^4 and R^5 are independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12} alkyl, halo-C_2-C_{12} alkenyl; halo-C_2-C_{12}-alkynyl; C_6-C_{14} aralkyl; C_1-C_{12} alkoxy; or C_1-C_{12} alkylthio;

R^6 and R^7 are independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12} alkyl; halo-C_2-C_{12} alkenyl; halo-C_2-C_{12} alkynyl; pyridyl; substituted pyridyl; phenyl; substituted phenyl; C_6-C_{14} aralkyl; substituted C_6-C_{14} aralkyl; C_1-C_{12} alkoxy or C_1-C_{12} alkylthio; or

R^2 and R^4 together with the carbon atoms to which they are bound form an optionally substituted C_5-C_6 cycloalkyl or cycloalkenyl ring; or

R^4 and R^6 together with the nitrogen and carbon atoms to which they are bound form a 3- to 7-membered ring optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkylthio or C_7-C_{16} aralkyl; or

R^6 and R^7 together with the nitrogen to which they are bound form a 3- to 7-membered ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy, nitro, C_1-C_6 alkyl, C_7-C_{16} aralkyl or C_1-C_6 alkylthio groups; and

n is 1, 2 or 3.

More preferably,

R^1 is hydrogen or hydroxy;

R^2 and R^3 are hydrogen;

R^4 and R^5 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; and

R^6 and R^7 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl, or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; or

R^4 and R^6 together with the nitrogen and carbon atoms to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1-C_6 alkyl; or

R^6 and R^7 together with the nitrogen to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1-C_6 alkyl; and

n is 1.

Particularly preferred compounds for use in the herbicidal compositions and method of this invention include:

3-(benzylamino)propane-1,1-bisphosphonic acid;

3-(1-pyrrolidino)propane-1,1-bisphosphonic acid;

3-(N-methyl-N-propylamino)propane-1,1-bisphosphonic acid;

3-(N-methyl-N-isobutylamino)propane-1,1-bisphosphonic acid;

3-(alpha-methylbenzylamino)propane-1,1-bisphosphonic acid;

3-(1-cyclohexylethylamino)propane-1,1-bisphosphonic acid;

(4-methyl-3-amino)pentane-1,1-bisphosphonic acid;

(4-methyl-3-benzylamino)pentane-1,1-bisphosphonic acid;

3-aminooctane-1,1-bisphosphonic acid;

4-(benzylamino)hexane-1,1-bisphosphonic acid;

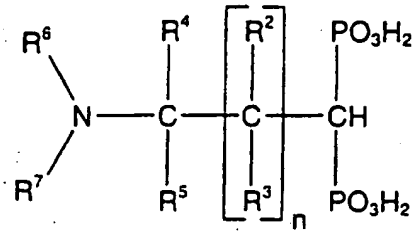
2-(2-pyrrolidino)ethane-1,1-bisphosphonic acid;

2-(2-piperidino)ethane-1,1-bisphosphonic acid;

2-[2-(4-methyl)piperidino]ethane-1,1-bisphosphonic acid; and

2-(2-pyrrolidino)-1-hydroxyethane-1,1-bisphosphonic acid.

In another aspect, this invention is directed to novel aza-bisphosphonic acid compounds of the Formula (II):



(II)

wherein

n is 1, 2, 3, 4, 5 or 6;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^2 and R^4 or R^4 and R^6 or R^6 and R^7 or R^4 and R^5 form an optionally substituted 3- to 7-membered ring as defined above;

m is 0, 1 or 2; and

agrochemically acceptable salts thereof;

with the proviso that when n is 1, at least one of R^2, R^3, R^4, R^5, R^6 and R^7 is not H.

Preferred novel compounds of Formula II are those in which

n is 1, 2 or 3;

R^2, R^3, R^4 and R^5 are each independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12}-alkyl; halo-C_2-C_{12}-alkenyl; halo-C_2-C_{12}-alkynyl; C_6-C14 aralkyl; C_1-C_{12} alkoxy; or C_1-C_{12} alkylthio;

R^6 and R^7 are each independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12}-alkyl; halo-C_2-C_{12}-alkenyl; halo-C_2-C_{12}-alknyl; C_6-C_{14} aralkyl; C_1-C_{12} alkoxy; or C_1-C_{12} alkylthio; or

R^2 and R^4 together with the carbon atoms to which they are bound form an optionally substituted C_5-C_6 cycloalkyl or cycloalkenyl ring; or

R^6 and R^7 together with the nitrogen to which they are bound form a 3- to 7-membered ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl; C_1-C_6 alkylthio or C_6-C_{10} aralkyl;

and agrochemically acceptable salts and hydrolyzable esters thereof.

More preferred novel compounds of Formula (II) are those wherein:

n is 1;

R^2 and R^3 are each hydrogen;

R^4 and R^5 are each independently hydrogen; C_1-C_8 alkyl: C_2-C_8 alkenyl; or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy;

R^6 and R^7 are each independently hydrogen; C_1-C_8 alkyl: C_2-C_8 alkenyl; or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; or

R^6 and R^7 together with the nitrogen to which they are bound form a piperidine or pyrrolidine ring optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C1-C_6 alkylthio or C_6-C_{10} aralkyl.

Specific compounds within the scope of this genus include:

3-(benzylamino)propane-1,1-bisphosphonic acid;

3-(1-pyrrolidino)propane-1,1-bisphosphonic acid;

3-(N-methyl-N-propylamino)propane-1,1-bisphosphonic acid;

3-(N-methyl-N-isobutylamino)propane-1,1-bisphosphonic acid;

3-(alphamethylbenzylamino)propane-1,1-bisphosphonic acid;

3-(1-cyclohexylethylamino)propane-1,1-bisphosphonic acid;

(4-methyl-3-amino)pentane-1,1-bisphosphonic acid;

(4-methyl-3-benzylamino)pentane-1,1-bisphosphonic acid;

3-aminooctane-1,1-bisphosphonic acid;

4-(benzylamino)hexane-1,1-bisphosphonic acid; and

2-(2-pyrrolidino)ethane-1,1-bisphosphonic acid.

The formulae given above are intended to include tautomeric forms of the structures drawn therein, as well as physically distinguishable modifications of the compounds which may arise, for example, from different ways in which the molecules are arranged in a crystal lattice, or from the inability of parts of the molecule to rotate freely in relation to other parts, or from geometrical isomerism, or form intra-molecular or inter-molecular hydrogen bonding, or otherwise.

The compounds of such formulae can exist in enantiomeric forms. The invention includes both individual enantiomers and mixtures of the two in all proportions.

As is employed herein, the term "hydrocarbyl", whether representing a substituent on its own or whether it is part of the definition of a larger group (e.g., as in hydrocarbyloxy, hydrocarbyl-$S(O)_m$-, etc.) is intended to include hydrocarbon groups having from 1 to 16 carbon atoms. The term hydrocarbyl therefore includes, for example, C_1 to C_{16} alkyl

including both straight and branched chain isomers (e.g., methyl, ethyl, propyl, isopropyl, sec-hexyl and hexyl); cycloalkyl of 3 to 16 carbon atoms (e.g., cyclopropyl, cyclobutyl and cyclohexyl); C_2 to C_{16} alkenyl including for example allyl and crotyl; C_2 to C_{16} alkynyl (e.g., propynyl); phenyl; phenylalkyl; alkylphenyl, alkenylphenyl, alkynylphenyl, alkylbenzyl, alkenylbenzyl, alkynyl benzyl, naphthyl and the like.

The term "substituted" when applied to the term "hydrocarbyl" (or to a similar term unless specifically defined otherwise) is intended to include hydrocarbyl groups, as defined above, having one or more substituents selected from the group consisting of halogen (i.e., fluorine, chlorine, bromine, and iodine); C_{1-10} alkyl, C_{1-10} alkoxy, C_{1-10} alkyl-$S(O)_m$-, nitro, cyano, or CF_3 groups. In the above definitions, m is 0, 1 or 2.

Further, when the hydrocarbyl radical is a substituted aryl radical (e.g., phenyl, benzyl or naphthyl), the substituents may include one or more of the substituents listed in the last foregoing paragraph. The term "substituted pyridyl" is intended to include those substituents detailed above for substituted aryl radicals.

In addition, unless specified otherwise, the term "alkyl" is intended to include straight chain, branched and cycloalkyl compounds. The above definitions the term "halogen" includes fluoro, chloro, bromo and iodo groups. In polyhalogenated groups the halogens may be the same or different.

The compounds of the present invention have been found to be active herbicides, possessing utility as postemergence herbicides and useful against a wide range of plant species including broadleaf and grassy species.

This invention therefore also relates to a method for controlling undesirable vegetation comprising applying to a locus where control of such vegetation is desired subsequent to the emergence of such vegetation a herbidically effective amount of a compound as described herein, together with an inert diluent or carrier suitable for use with herbicides.

The terms "herbicide" and "herbicidal" are used herein to denote the inhibitive control or modification of undesired plant growth. Inhibitive control and modification include all deviations from natural development such as, for example, total killing, growth retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation, leaf burn and dwarfing. The term "herbicidally effective amount" is used to denote any amount which achieves such control or modification when applied to the undesired plants themselves or to the area in

which these plants are growing. The term "plants" is intended to include germinated seeds, emerging seedlings and established vegetation, including both roots and above-ground portions.

The term "agriculturally acceptable salt" is easily determined by one of ordinary skill in the art and includes alkali metal, ammonium, phosphonium, sulfonium salts, organic derivatives thereof, and the like.

The compounds of this invention wherein R^1 is hydrogen and n is 0 may generally be prepared by reacting tetraethyl vinylidene bisphosphonate with an appropriate amine. Such reaction is typically carried out at between about 0° and about 100° C in the presence of a suitable nonreactive solvent, such as acetonitrile, diethyl ether, toluene, tetrahydrofuran, and the like. The ester groups may then be removed using bromotrimethylsilane or aqueous hydrochloric acid.

Tetraethyl vinylidene bisphosphonate may be prepared in accordance with the method disclosed by C. Degenhardt et al., J. Org. Chem., Vol 51, pp 3488-3490 (1986). The amines employed are either commercially available or may be prepared by means well known to one of skill in the art, e.g., preparation from the corresponding bromides by a Gabriel Synthesis (see Vogel, "A Textbook of Practical Organic Chemistry", 3d Ed., pp 569).

The compounds of this invention wherein R^1 is hydrogen and n is not 0 may be generally prepared by alkylation of tetraethyl methylene bisphosphonate with a substituted alkyl halide, such as allyl bromide, ethyl bromoacetate or N,N-dimethyl chloroacetamide and subsequent conversion of the olefin, ester or amide to an amine and hydrolysis of the phosphonate esters to phosphonic acids.

Alternatively, for compounds where R^1=H and n=1, the compounds may be prepared by adding a nitroalkane to vinylidine bisphosphonate. This intermediate nitro compound may be reduced to the primary amine from which various substituted amines can be produced by reductive alkylation. On the other hand, the nitro group may be hydrolyzed to give a ketone which can be reductively aminated to give various amines.

For the production of compounds wherein the amine contains sensitive groups, the phosphonate ester groups may first be transesterified by the use of a compound such as bromotrimethylsilane. Such groups can be subsequently unblocked by hydrolysis with water.

Alternatively, for producing compounds wherein R^1 is other than H, the appropriate carboxylic acid, amide or nitrile can be converted employing PCl_3 and phosphorous acid or P_2O_3 utilizing means well known to those of skill in the art.

The compositions of this invention comprise a compound of Formula (I) above and a suitable carrier, which carriers are well known to one of ordinary skill in the art.

The compounds of the present invention are useful as herbicides and can be applied in a variety of ways known to those skilled in the art, at various concentrations. The compounds are useful in controlling the growth of undesirable vegetation by post-emergent application to the locus where control is desired. In practice, the compounds are applied as formulations containing the various adjuvants and carriers known to or used in the industry for facilitating dispersion. The choice of formulation and mode of application for any given compound may affect its activity, and selection will be made accordingly. The compounds of the invention may thus be formulated as wettable powders, as emulsifiable concentrates, as powders or dusts, as flowables, as solutions, suspensions or emulsions, or in controlled-release forms such as microcapsules. These formulations may contain as little as about 0.5% to as much as about 95% or more by weight of active ingredient. The optimum amount for any given compound will depend upon the nature of plants to be controlled. The rate of application will generally vary from about 0.01 to about 10 pounds per acre, preferably from about 0.02 to about 4 pounds per acre.

Wettable powders are in the form of finely divided particles which disperse readily in water or other liquid carriers. The particles contain the active ingredient retained in a solid matrix. Typical solid matrices include fuller's earth, kaolin clays, silicas and other readily wettable organic or inorganic solids. Wettable powders normally contain about 5% to about 95% of the active ingredient plus a small amount of wetting, dispersing, or emulsifying agent.

Emulsifiable concentrates are homogeneous liquid compositions dispersible in water or other liquid, and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone and other nonvolatile organic solvents. In use, these concentrates are dispersed in water or other liquid and normally applied as a spray to the area to be treated. The amount of active ingredient may range from about 0.5% to about 95% of the concentrate.

Dusts are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers.

Microcapsules are typically droplets or solutions of the active material enclosed in an inert porous shell which allows escape of the enclosed material to the surrounds at controlled rates. Encapsulated droplets are typically about 1 to 50 microns in diameter. The enclosed material typically constitutes about 50 to 95% of the weight of the capsule, and may include solvent in addition to the active compound. Shell of membrane materials include natural and synthetic rubbers, cellulosic materials, styrene-butadiene copolymers, polyacrylonitriles, polyacrylates, polyesters, polyamides, polyureas, polyurethanes and starch xanthates.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentration, such as water, acetone, alkylated naphthalenes, xylene and other organic solvents. Pressurized sprayers, wherein the active ingredient is dispersed in finely-divided form as a result of vaporization of a low boiling dispersant solvent carrier may also be used.

Many of these formulations include wetting, dispersing or emulsifying agents. Examples are alkyl and alkylaryl sulfonates and sulfates and their salts; polyhydric alcohols; polyethoxylated alcohols; esters and fatty amines. These agents when used normally comprise from 0.1% to 15% by weight of the formulation.

Each of the above formulations can be prepared as a package containing the herbicide together with other ingredients of the formulation (diluents, emulsifiers, surfactants, etc.). The formulations can also be prepared by a tank mix method, in which the ingredients are obtained separately and combined at the grower site.

The compounds of the present invention are also useful when combined with other herbicides and/or defoliants, desiccants, growth inhibitors, and the like. These other materials can comprise from about 5% to about 95% of the active ingredients in the formulations. These combinations frequently provide a higher level of effectiveness in controlling weeds and often provide results unattainable with separate formulations of the individual herbicides.

Examples of other herbicides, defoliants, desiccants and plant growth inhibitors with which the compounds of this invention can be combined are:

A. Benzo-2,1,3-thiadiazin-4-one-2,2-dioxides such as bentazone;

B. hormone herbicides, particularly the phenoxyalkanoic acids such as MCPA, MCPA-thioethyl, dichlorprop, 2,4,5-T, MCPB, 2,4-D,2,4-DB, mecoprop, trichlopyr, fluroxypyr, clopyralid, and their derivatives (e.g. salts, esters and amides);

C. 1,3-dimethylpyrazole derivatives such as pyrazoxyfen, pyrazolate and benzofenap;

D. Dinitrophenols and their derivatives (e.g. acetates such as DNOC, dinoterb, dinoseb and its ester, dinoseb acetate;

E. dinitroaniline herbicides such as dinitramine, trifluralin, ethalfluralin, pendimethalin; and oryzalin;

F. arylurea herbicides such as diuron, flumeturon, metoxuron, neburon, isoproturon, chlorotoluron, chloroxuron, linuron, monolinuron, chlorobromuron, daimuron, and methabenzthiazuron;

G. phenylcarbamoyloxyphenylcarbamates such as phenmedipham and desmedipham;

H. 2-phenylpyridazin-3-ones such as chloridazon, and norflurazon;

I. uracil herbicides such as lenacil, bromacil and termacil;

J. triazine herbicides such as atrazine, simazine, aziprotryne, cyanazine, prometryn, dimethametryn, simetryne, and terbutryn;

K. phosphorothioate herbicides such as piperophos, bensulide, and butamifos;

L. thiolcarbamate herbicides such as cycloate, vernolate, molinate, thiobencarb, butylate*, EPTC*, triallate, diallate, ethyl esprocarb, tiocarbazil, pyridate, and dimepiperate;

M. 1,2,4-triazin-5-one herbicides such as metamitron and metribuzin;

N. benzoic acid herbicides such as 2,3,6-TBA, dicamba and chloramben;

O. anilide herbicides such as pretilachlor, butachlor, the corresponding alachlor, the corresponding compound propachlor, propanil, metazachlor, metolachlor, acetochlor, and dimethachlor;

P. dihalobenzonitrile herbicides such as dichlobenil, bromoxynil and ioxynil;

Q. haloalkanoic herbicides such as dalapon, TCA and salts thereof;

R. Diphenylether herbicides such as lactofen, fluroglycofen or salts or esters thereof, nitrofen, bifenox, acifluorfen and salts and esters thereof, oxyfluorfen and fomesafen; chlornitrofen and chlomethoxyfen;

S. phenoxyphenoxypropionate herbicides such as diclofop and esters thereof such the methyl ester, fluazifop and esters thereof, haloxyfop and esters thereof, quizalofop and esters thereof and fenoxaprop and esters thereof such as the ethyl ester;

T. triketone and cyclohexanedione herbicides such as alloxydim and salts thereof, sethoxydim, cycloxydim, sulcotrione, tralkoxydim, and clethodim;

U. Sulfonyl urea herbicides such as chlorosulfuron, sulfometuron, metsulfuron and esters thereof; benzsulfuron and esters thereof such as the ester thereof methyl, DPX-M6313, chlorimuron and esters such as the ethyl ester thereof, pirimisulfuron and esters such as the methyl ester thereof, DPX-LS300 and pyrazosulfuron;

V. Imidazolidinone herbicides such as imazaquin, imazamethabenz, imazapyr and isopropylammonium salts thereof, imazathapyr;

W. arylanilide herbicides such as flamprop and esters thereof, benzoylprop-ethyl, diflufenican;

X. amino acid herbicides such as glyphosate and gluyfosinate and their salts and esters, sulphosate, and bilanafos;

Y. organoarsenical herbicides such as MSMA;

Z. herbicidal amide derivative such as napropamide, propyzamide, carbetamide, tebutam, bromobutide, isoxaben, naproanilide, diphenamid, and naptalam;

AA. miscellaneous herbicides including ethofumesate, cinmethylin, difenzoquat and salts thereof such as the methyl sulfate salt, clomazone, oxadiazon, bromofenoxim, barban, tridiphane, (in the ratio 3:1) flurochloridone, quinchlorac and mefanacet;

BB. examples of useful contact herbicides include bipyridylium herbicides such as those in which the active entity is paraquat and those in which the active entity is diquat.

* These compounds are preferably employed in combination with a safener such as 2,2-dichloro-N,N-di-2-propenylacdtamide (dichlormid).

These formulations can be applied to the areas where control is desired by conventional methods. Dust and liquid compositions, for example, can be applied by the use of powerdusters, boom and hand sprayers and spray dusters. The formulations can also be applied from airplanes as a dust or a spray or by rope wick appiications.

The following are examples of typical formulations:

5% dust: 5 parts active compound
95 parts talc

2% dust: 2 parts active compound
1 part highly dispersed silicic acid
97 parts talc

These dusts are formed by mixing the components then grinding the mixture to the desired particle size.

Wettable powders:

70%: 70 parts active compound
5 parts sodium dibutylnaphthylsulfonate
3 parts naphthalenesulfonic acid/phenolsulfonic acid/phenol-sulfonic acid/formaldehyde condensate (3:2:1)
10 parts kaolin
12 parts Champagne chalk

40%: 40 parts active compound
5 parts sodium lignin sulfonate
1 part sodium dibutylnaphthalene sulfonic acid
54 parts silicic acid

25% 25 parts active compound
4.5 parts calcium lignin sulfate
1.9 parts Champagne chalk/-hydroxyethyl cellulose (1:1)
8.3 parts sodium aluminum silicate
16.5 parts kieselguhr
46 parts kaolin

10% 10 parts active compound
3 parts of a mixture of sodium salts of saturated fatty alcohol sulfates
5 parts naphthalenesulfonic acid/formaldehyde condensate
82 parts kaolin

These wettable powders are prepared by intimately mixing the active compounds with the additives in suitable mixers. and grinding the resulting mixture in mills or rollers.

Emulsifiable concentrate:

25% 25 parts active substance

2.5 parts epoxidized vegetable oil

10 parts of an alkylarylsulfonate/fatty alcohol polyglycol ether mixture

57.5 parts xylene

The amount of the present compositions which constitute a herbicidally effective amount depends upon the nature of the seeds or plants to be controlled. The rate of application of active ingredients varies from about 0.01 to about 25 pounds per acre, preferably about 0.10 to about 10 pounds per acre with the actual amount depending on the overall costs and the desired results. It will be readily apparent to one skilled in the art tha. compositions exhibiting lower herbicidal activity will require a higher dosage than more active compounds for the same degree of control.

EXAMPLES

The following examples are intended to further illustrate the present invention and are not intended to limit the scope of this invention in any manner whatsoever.

EXAMPLE 1

Preparation of 3-(dipropylamino) propane-1,1-bisphosphonic acid (Compound No. 17)

A. Preparation of 3,3-bis(diethoxylphosphinyl)-propanoic acid

A solution of NaOH (4.00 g, 100 mmol) in water (50 ml) was added to a solution of ethyl 3,3-bis(diethoxyphosphinyl)propionate (32.6 g, 87 mmol) in EtOH (100 ml), and heated at 80°C for 1 hour. After cooling, the EtOH was evaporated, and the residue was acidified to methyl orange with 12 N HCl. The product was extracted into dichloromethane (5x50 ml). The organic layer was dried (Na_2SO_4) and concentrated to give the title compound (28.8 g, 96%) as a viscous oil.

B. Preparation of N,N-dipropyl-3,3-bis(diethoxy-phosphinyl)propionamide

To a solution of 3.3-bis(diethoxyphosphinyl)-propanoic acid (1.5 g, 4.34 mmol) and dimethylformamide (2 drops) in dichloromethane (10 ml) was added oxalyl chloride (0.61 g., 4.77 mmol). The solution was stirred at ambient temperature until gas evolution ceased (– 1

hour). The solution was evaporated and pumped under vacuum to give the acid chloride as an orange oil, which was used directly.

The acid chloride from above was dissolved in dichloromethane (20 ml) and cooled to 0°C. A solution of dipropylamine (0.89 g, 8.8 mmol) in dichloromethane (5 ml) was added dropwise, allowed to warm to room temperature, and stirred for 18 hours. Dichloromethane (25 ml) was added and the reaction mixture washed with 1N HCl (25 ml) and $NaHCO_3$ (25 ml). The organic layer was dried (Na_2SO_4) and concentrated to give the title compound (1.3 g, 70%) as an oil.

C. Preparation of tetraethyl-3-(dipropylamino)-propane-1,1-bisphosphonate

A solution of N,N-dipropyl-3,3-bis(diethoxyphosphinyl)propionamide (1.25 g, 2.9 mmol) in THF (7.1 ml) was cooled to 0°C, and borane-methylsulfide (0.71 ml, 7.1 mmol) was added via syringe. The reaction was stirred at 0°C for 20 minutes, then warmed at 65 C for 3 hours. The reaction mixture was cooled to 0°C and 6N HCl (6 ml) was added carefully. The solvent was removed *in vacuo*, and the residue was treated with methanol (5 ml) and concentrated. The residue was dissolved in water (10 ml) and extracted with Et_2O (3 x 10 ml). The aqueous layer was made basic to phenolphthalein with solid KOH and saturated with NaCl. The product was extracted into dichloromethane (5 x 20 ml), dried (Na_2SO_4) and concentrated to give the title compound (0.71 g, 60%).

D. Preparation of 3-(dipropylaminopropane-1,1-bisphosphonic acid.

Tetraethyl 3-(dipropylamino)propane-1,1-bisphosphonate (0.55 g, 1.3 mmol) and 12NHCl (6 ml) were heated at reflux for 20 hours. After cooling, the volatile materials were removed under vacuum to give 0.47 g of Compound No. 17 as a hygroscopic glass.

EXAMPLE 2

Preparation of 3-(benzylamino)pentane-1,1-bisphosphonic acid (Compound No. 21)

A. Preparation of N-methoxy-N-methyl-3,3-bis-(diethoxyphosphinyl)propionamide.

To a solution of 3,3-bis(diethoxyphosphinyl)propanoic acid (4.00 g, 11.5 mmol) and dimethylformamide (2 drops) in dichloromethane (25 ml) was added oxalyl chloride (1.65 g, 13.0 mmol). The solution was stirred at ambient temperature until gas evolution ceased (~1 hour). The solution was evaporated and benzene (20 ml) was added. The solvent was removed under vacuum to give the acid chloride as an orange oil, which was used directly.

The acid chloride from above was dissolved in dichloromethane (100 ml) and N-methyl-O-methylhydroxylamine hydrochloride (1.25 g, 13.0 mmol) was added. The reaction mixture was cooled in an ice bath and pyridine (2.05 g, 26.0 mmol) was added dropwise. After the addition, the reaction mixture was allowed to warm to room temperature for 1 hour. This mixture was washed with 1N HCl (50 ml) and saturated $NaHCO_3$ (50 ml), dried (Na_2SO_4) and concentrated to give the crude product as an oil. Flash chromatography on silica gel eluting with 20% *i*-propanol in EtOAc gave the title compound (3.50 g, 78%) as a light yellow oil.

B. Preparation of tetraethyl 3-oxopentane-1,1-bisphosphonate

A solution of N-methoxy-N-methyl-3,3-bis(diethoxyphosphinyl)propionamide (1.00g, 2.6 mmol) in THF (5 ml) was slowly added to a slurry of 80% sodium hydride (80 mg, 2.7 mmol) in THF (10 ml) at 0°C. Stirring was continued until all of the hydride was consumed (~20 minutes). The solution was cooled to -78°C and ethylmagnesium bromide (1.0 ml of a 3.0M solution in diethyl ether, 3.0 mmol) was added. After the addition, the reaction mixture was warmed to 0°C and stirred for one hour. The reaction was quenched by pouring slowly into a well-stirred ice-cold mixture of ethanol (40 ml) and concentrated HCl (5 ml). The solvents were removed *in vacuo*, the residue was taken up in brine (20 ml) and extracted with dichloromethane (4X20 ml). The combined extracts were dried (Na_2SO_4), concentrated *in vacuo*, and the resulting oil was purified by flash chromatography on silica gel eluting with 10% *i*-propanol in ethyl acetate to give the title compound (0.50 g, 54%) as a pale yellow oil.

C. Preparation of 3-(benzylamino)pentane-1,1-bisphosphonic acid.

To a stirred solution of tetraethyl 3-oxopentane-1,1-bisphosphonate (0.50 g, 1.4 mmol) in methanol (5 ml) was added a small amount of bromothymol blue and benzylamine (0.75 g, 7.0 mmol). Acetic acid was added dropwise until the solution turned yellow (pH=6), and $NaCNBH_3$ (57 mg, 0.9 mmol) was added. The resulting yellow solution was stirred at room temperature for 2 days, at which time more $NaCNBH_3$ (20 mg) was added. After stirring a total of 4 days, the reaction was quenched by adding concentrated HCl until the pH was less than 1, and the solvents were removed *in vacuo*. The residue was taken up in water (10 ml) and washed with diethyl ether (2x20 ml). The aqueous layer was made basic (pH greater than 10) by the addition of solid KOH, saturated with NaCl, and extracted with

dichloromethane (5x25 ml). The combined extracts were dried (Na_2SO_4) and concentrated to give tetraethyl 3-benzylaminopentane-1,1-bisphosphonate. This material was hydrolyzed by heating at reflux in concentrated HCl (6ml) for 20 hours. The volatiles were removed under vacuum, the residue dissolved in water (10ml) and concentrated under vacuum to give 0.49 g of Compound No. 21 as a hygroscopic foam.

EXAMPLE 3

Preparation of 3-(butylamino)propane-1,1-bisphosphonic acid (Compound No. 20)

A. Preparation of N-butyl-3,3-bis(diethoxyphosphinyl)propionamide

Tetraethyl methylenebisphosphonate (1.44 g, 5.0 mmol) in THF (1 mL) was added to a slurry of 80% sodium hydride (150 mg, 5.0 mmol) in THF (4 mL) at 0°C. The reaction was warmed to room temperature and stirred until all of the hydride was consumed. A solution of N-butyl-2-chloroacetamide (0.75 g, 5.0 mmol) in THF (1 ml) and potassium iodide (100 mg) were then added. The reaction mixture was then heated at 50°C for 18 hours, during which time sodium chloride precipitated. Additional sodium hydride (20 mg) was added, and the reaction mixture was heated an additional 4 hours. After cooling, the mixture was poured into 1N HCl (10 mL) and diethyl ether (50 mL) was added. The diethyl ether layer was further extracted with water (3x10 mL). The combined aqueous fractions were extracted with dichloromethane (4x25 mL). The combined extracts were dried (Na_2SO_4) and concentrated to give the title compound (1.40 g, 70%) as an oil.

B. Preparation of 3-(butylamino)propane-1,1-bisphosphonic acid.

A solution of N-butyl-3,3-bis(diethoxyphosphinyl)propionamide (1.40 g, 3.5 mmol) in THF (9 mL) was cooled to 0°C, and borane-methyl sulfide (0.90 ml, 9.0 mmol) was added via syringe. The reaction was stirred at 0°C for 5 minutes, then warmed to 65°C for 3 hours. The reaction mixture was cooled to 0°C and 6N HCl (6ml) was added carefully. The solvent was removed *in vacuo*, and the residue was repeatedly concentrated from methanol (3x10 mL). The product was dissolved in 12 N HCl and heated at reflux for 20 hours. After cooling, the volatile materials were removed under vacuum, the residue was dissolved in water (10 mL) and then concentrated to give 1.05g of Compound No. 20 as a hygroscopic glass.

EXAMPLE 4

Preparation of 2-(2-pyrrolidino)ethane-1,1-bisphosphonic acid, triammonium salt (Compound No. 107)

A. Preparation of tetraethyl 2[2-(1-pyrrolino)]ethane-1,1-bisphosphonate

A solution of N-methoxy-N-methyl-3,3-bis(diethoxyphosphinyl)propionamide (1.82 g, 4.7 mmol) in THF (5 ml) was slowly added to a slurry of 80% sodium hydride (160 mg, 5.3 mmol) in THF (15 ml) at 0°C. Stirring was continued until all of the hydride was consumed (~20 minutes). The solution was cooled to 0°C and 3-[1-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)]propylmagnesium bromide (15 ml of a 1.0M solution in diethyl ether, 15 mmol) was added. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 15 hours. At that time, the mixture was cooled to 0°C and quenched by the slow addition of 10% HCl, and stirred at room temperature for 2 hours. Ether (30 mL) was added and the product was extracted with 1N HCl (3x10 mL). The combined aqueous extracts were washed with ether (10 mL) and then solid KOH was added to bring the pH to 10. The solvent was evaporated and the residue extracted with dichloromethane (4x50 mL). Evaporation of the solvent gave the crude product which was purified by flash chromatography on silica gel eluting with 5% methanol in chloroform to give the title compound (0.40 g).

B. Preparation of tetraethyl 2-(2-pyrrolidino)ethane-1,1-bisphosphonate.

Tetraethyl 2-[2-(1-pyrrolino)]ethane-1,1-bisphosphonate (0.40 g, 1.15 mmol) was dissolved in ethanol (4 mL) and $NaCNBH_3$ (80 mg, 1.25 mmol) was added. 6N HCl was added to keep the solution acidic to bromocresol green (pH~4). After 30 minutes, 6 N HCl was added (2 mL) and the solvent was removed *in vacuo*. Methanol (10 ml) was added and evaporated. The residue was added to dichloromethane (20 mL) and extracted into 1N HCl (2x10 mL). The solution was made basic (pH~10) with solid KOH and the product was extracted into dichloromethane (3x20 ml). The combined organic extracts were dried (K_2CO_3) and concentrated to give 0.26 g of tetraethyl 2-(2-pyrrolidino)ethane-1,1-bisphosphonate.

C. Preparation of 2-(2-pyrrolidino)ethane-1,1-bisphosphonic acid, triammonium salt.

To a stirred solution of tetraethyl 2-(2-pyrrolidino)ethane-1,1-bisphosphonate (0.26 g, 0.75 mmol) in dry dichloromethane (0.5 mL) at 0°C was added bromotrimethylsilane (1.00 mL, 8.0 mmol), and the solution was allowed to warm to room temperature. After stirring for 16 hours, the solvent was removed *in vacuo*, the residue was dissolved in benzene (7 mL) and concentrated *in vacuo*. To the residue was added NH_4OH (4 mL of a 3.5 M solution) which was stirred for 30 minutes at room temperature. The solvent was removed *in vacuo*, and the residue concentrated repeatedly from methanol (2x5 mL) to give 0.24 g of 2-(2-pyrrolidino)ethane-1,1-bisphosphonic acid as a white powder.

EXAMPLE 5

Preparation of 5-aminopentane-1,1-bisphosphonic acid, triammonium salt (Compound No. 110)

A. Preparation of tetraethyl 5-aminopentane-1,1-bisphosphonate.

Tetraethyl vinylidine bisphosphonate (1.20 g, 4.0 mmol) was dissolved in dry THF (10 mL) and cooled to 0°C. A solution of 3-[1-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)]propylmagnesium bromide in ether (4.5 mL of 1.0 M solution, 4.5 mmol) was added slowly and the reaction mixture was then allowed to warm to room temperature for 15 hours. The reaction was quenched with 1N HCl (25 mL) and stirred for 2 hours. This was washed with ether (10 mL). The ether layer was extracted with 1N HCl and the combined aqueous extracts were made basic (pH=10) with solid KOH. Volatiles were removed *in vacuo*, and the residue was extracted with dichloromethane (3x50 mL). The solution was concentrated to 20 mL and extracted with 1N HCl (2x10 mL). Solid KOH was added to pH=10, and the product was extracted into dichloromethane (3x15 mL). The solution was dried (K_2CO_3) and concentrated to give the title compound (0.54 g) as an oil.

B. Preparation of 5-aminopentane-1,1-bisphosphonic acid, triammonium salt.

To a stirred solution of tetraethyl 5-aminopentane-1,1-bisphosphonate (0.51 g, 1.5 mmol) in dry dichloromethane (0.5 mL) at 0°C was added bromotrimethylsilane (1.3 mL, 10 mmol), and the solution was allowed to warm to room temperature. After stirring for 16 hours, the solvent was removed *in vacuo*, the residue was dissolved in benzene (5 mL) and concentrated *in vacuo*. To the residue was added NH_4OH (7 mL of a 3.0 M solution) which

was stirred for 30 minutes at room temperature. The solvent was removed *in vacuo*, and the residue concentrated repeatedly from methanol (2x5 mL) to give 0.52 g of 5-amino-1,1-pentylbisphosphonic acid, triammonium salt as a white powder.

EXAMPLE 6

Preparation of N-benzyl-5-aminopentane-1,1-bisphosphonic acid, triammonium salt (Compound No. 111).

A. Preparation of tetraethyl N-benzoyl-5-aminopentane-1,1-bisphosphonate.

A solution of benzoyl chloride (0.73 g, 5.0 mmol) in dichloromethane was added slowly to a solution of tetraethyl 5-aminopentane-1,1-bisphosphonate (1.50 g, 4.5 mmol) from Example 11, part A, and triethylamine (0.76 mL, 5.5 mmol) in dichloromethane at 0°C. After warming to room temperature for 30 minutes, the reaction was quenched by addition of 1N HCl (30 mL). The product was extracted into dichloromethane (2x20 mL) and the combined organic layers were washed with saturated $NaHCO_3$ (2x15 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Flash chromatography on silica gel eluting with 15% i-propanol in ethylacetate in EtOAc gave the title compound (0.64 g) as an oil.

B. Preparation of tetraethyl N-benzyl-5-aminopentane-1,1-bisphosphonate.

A solution of tetraethyl N-benzoyl-5-aminopentane-1,1-bisphosphonate (0.63 g, 1.36 mmol) in THF (3.4 mL) was cooled to 0°C, and borane methylsulfide (0.34 ml, 3.4 mmol) was added via syringe. The reaction was stirred at 0°C for 20 minutes, then warmed to 65°C for 2.5 hours. The reaction mixture was cooled to 0°C and 6N HCl (4.0 ml) was added carefully. The solvent was removed *in vacuo*, and the residue was concentrated repeatedly from methanol (2x5 mL). The residue was dissolved in water (10 ml) and extracted with diethyl ether (3x5 ml). The aqueous layer was made basic to phenolphthalein with solid KOH and saturated with NaCl. The product was extracted into dichloromethane (5x20 ml), dried (Na_2SO_4) and concentrated to give the title compound (0.28 g).

C. Preparation of N-benzyl-5-aminopentane-1,1-bisphosphonic acid, triammonium salt.

Bromotrimethylsilane (0.54 mL, 4.1 mmol) was added to a stirred solution of the compound of part B (0.26 g, 0.58 mmol) in dry dichloromethane (0.5 mL) at 0°C, and the solution was allowed to warm to room temperature. After stirring for 18 hours, the solvent was removed *in vacuo*. To the residue was added NH_4OH (7 mL of a 3.0 M solution) which

was stirred for 30 minutes at room temperature. The solvent was removed *in vacuo*, and the residue concentrated repeatedly from methanol (2x5 mL) to give 0.32 g N-benzyl-5-aminopentane-1,1-bisphosphonic acid, triammonium salt as a white powder.

EXAMPLE 7

Preparation of 3-aminooctane-1,1-bisphosphonic acid (Compound No. 119).

A. Preparation of tetraethyl 3-nitrooctane-1,1-bisphosphonate

A solution of tetraethyl vinvylidinebisphosphonate (2.0 g, 6.67 mmol) in THF (3 ml) was added dropwise to a stirred solution of 1-nitrohexane (0.87 g, 6.67 mmol) and diisopropylamine (0.76 g, 7.50 mmol) in THF (4 mL) at room temperature. The reaction mixture was stirred at ambient temperature for 18 hours, and then heated at 50°C for 3 hours. After cooling, the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (30 mL) and washed with 1N HCl (10 mL) and water (10 mL). The combined aqueous layers were extracted with dichloromethane (10 mL). The organic layers were pooled, dried (Na_2SO_4) and concentrated. Flash chromatography on silica gel eluting with 5% methanol in chloroform gave the title compound (2.3 g, 80%) as an oil.

B. Preparation of tetraethyl 3-aminooctane-1,1-bisphosphonate.

To a stirred solution of tetraethyl 3-nitrooctane-1,1-bisphosphonate (0.70 g, 1.62 mmol) in methanol (4 mL) was added ammonium formate (0.45 g, 6.9 mmol) and 10% palladium on carbon (0.070 g). After 24 hours, more 10% palladium on carbon (0.035 g) and ammonium formate (0.45 g, 6.9 mmol) were added. After stirring for a total of 4 days, the reactior. mixture was filtered, rinsing the residue with methanol, and concentrated. The residue was taken up in brine (5 mL) and extracted with dichloromethane (4x15 mL), dried (Na_2SO_4) and concentrated to give the title compound (0.60 g, 95%) as an oil.

C. Preparation of 3-aminooctyl-1,1-bisphosphonic acid, triammonium salt.

To a solution of tetraethyl 3-aminooctane-1,1-bisphosphonate (0.45 g, 1.12 mmol) in dry dichloromethane (1.1 mL) was added bromotrimethylsilane (1.05 mL, 7.85 mmol) via syringe. After 18 hours, the mixture was concentrated under vacuum. To the residue was added 3N NH_4OH (8 mL) which was stirred for 30 minutes at room temperature. The solvent was removed in vacuo and the residue concentrated from methanol (2 mL) to give 0.40 g of 3-aminooctane-1,1-bisphosphonic acid, triammonium salt as a white powder.

Employing a process similar to those described above, the following compounds, listed in Tables I - IV, were prepared:

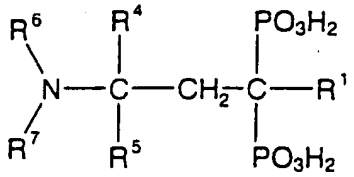


TABLE I

Comp. No.	R^1	R^4	R^5	R^6	R^7
2	H	H	H	H	Phenyl [Ph]
7	H	H	H	H	H
14*	H	H	H	H	$-C_2H_5$
15	H	H	H	H	$-nC_3H_7$
17	H	H	H	$-nC_3H_7$	$-nC_3H_7$
18	H	H	H	H	$-CH(CH_3)_2$
19	H	H	H	H	benzyl
20	H	H	H	H	$-nC_4H_9$
21	H	$-C_2H_5$	H	H	benzyl
23	H	H	H	H	$-CH_2CH(CH_3)_2$
24	H	H	H	$-CH_3$	benzyl
25	H	H	H	H	cyclopropyl
26	H	H	H	$-C_2H_5$	$-C_2H_5$
27	H	H	H	H	2-methylbenzyl
28	H	H	H	H	cyclohexyl
29	H	H	H	$-CH_3$	$-nC_3H_7$
31	-OH	H	H	H	H
36	-OH	H	H	$-CH_3$	benzyl
37	-OH	H	H	$-C_2H_5$	$-C_2H_5$
38	-OH	H	H	H	$-CH_2CH_2OCH_2CH_3$
39	-OH	H	H	H	$-iC_3H_7$
40	-OH	H	H	$-CH_2CH_2OCH_2CH_3$	$-CH_2CH_2OCH_2CH_3$

TABLE I

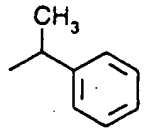
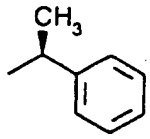
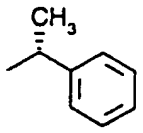
Comp. No.	R^1	R^4	R^5	R^6	R^7
41	-OH	H	H	H	-nC_3H_7
42	-OH	H	H	-CH_3	-nC_5H_{11}
43	-OH	H	H	H	-C_2H_5
44	-OH	H	H	-CH_3	-CH_3
45	-OH	H	H	-CH_3	-nC_3H_7
46	-OH	H	-iC_3H_7	H	-CH_3
47	-OH	H	-iC_3H_7	H	benzyl
52	-OH	H	H	H	-iC_3H_7
53	-OH	H	H	-CH_3	cyclohexyl
54	-OH	H	-iC_3H_7	H	2,4-dichlorobenzyl
55	-OH	H	H	H	-$CH(CH_3)CH_2CH_3$
56	-OH	H	H	-CH_3	-$CH(CH_3)CH_2CH_3$
57	-OH	H	H	-C_2H_5	-nC_3H_7
58	-OH	H	H	-nC_3H_7	-nC_3H_7
60	-OH	H	H	H	
61	-OH	H	H	H	
62	-OH	H	H	H	
63	-OH	H	-nC_3H_7	H	benzyl
64	-OH	H	-iC_3H_7	H	4-methoxybenzyl
65	-OH	H	-nC_3H_7	H	3-trifluoromethylbenzyl
66	-OH	H	-iC_3H_7	H	3-trifluoromethylbenzyl
68	-OH	H	-nC_3H_7	H	3-methoxybenzyl
69	-OH	H	-nC_3H_7	H	-nC_3H_7

TABLE I

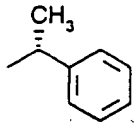
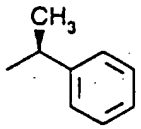
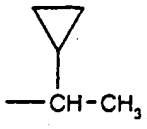
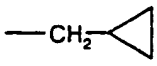
Comp. No.	R^1	R^4	R^5	R^6	R^7
70	-OH	H	-iC_4H_9	H	benzyl
71	-OH	H	H	H	benzyl
72	-OH	H	-iC_3H_7	H	2-chlorobenzyl
73	-OH	H	-CH_3	H	benzyl
74	-OH	H	-C_2H_5	H	benzyl
75	-OH	H	-iC_3H_7	H	4-chlorobenzyl
76	H	H	H	H	-$CH(CH_3)CH_2CH_3$
78	H	H	H	H	
79	H	H	H	H	
81	H	H	H	H	-C_6H_{13}
82	H	H	H	H	-$CH_2CH_2CH_2CH_2$-Ph
83	H	H	-C_2H_5	H	H
84	H	H	H	H	
85	H	H	H	H	-$CH_2CH_2CH_2$-Ph
86	H	H	H	H	-$CH(CH_3)$-Ph
87	H	H	H	H	4-methylbenzyl
88	H	H	H	H	4-chlorobenzyl
89	H	H	H	H	-CH_3
90	H	H	H	H	-$CH_2CH_2CH(CH_3)_2$
91	H	H	H	H	2-chlorobenzyl
92	H	H	H	H	4-phenylbenzyl
93	H	H	H	H	
94	H	H	H	H	-$CH(CH_3)CH(CH_3)_2$

TABLE I

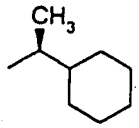
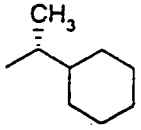
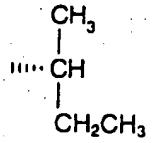
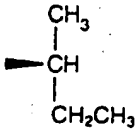
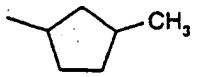
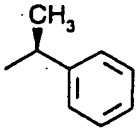
Comp. No.	R^1	R^4	R^5	R^6	R^7
95	H	H	H	H	$-CH_2CH(CH_3)_2$
96	H	H	H	$-nC_3H_7$	benzyl
97	H	H	H	$-nC_3H_7$	$-CH_2CH(CH_3)_2$
98	H	H	H	$-C_2H_5$	$-nC_3H_7$
99	H	H	H	H	
100	H	H	H	H	
101	H	H	$-CH_3$	H	$-nC_4H_9$
102	H	H	H	H	
103	H	H	H	H	
104	H	H	H	H	$-nC_5H_9$
105	H	H	H	H	
106	H	H	$-C_2H_5$	H	2-chlorobenzyl
108	H	H	$-C_2H_5$	H	
109	H	H	$-C_2H_5$	H	$-nC_4H_9$
118	H	nC_3H_7	H	H	benzyl
119	H	H	$-nC_5H_{11}$	H	H
120	H	H	$-iC_3H_7$	H	H

TABLE I

Comp. No.	R^1	R^4	R^5	R^6	R^7
121	H	H	H	H	$-CH_2CH_2CH_2OH$
122	H	$-iC_3H_7$	H	H	benzyl
123	H	H	$-nC_3H_7$	H	H
124	H	H	benzyl	H	H
125	H	$-CH_3$	H	H	H
126	H	$-CH_3$	$-CH_3$	H	H
127	H	H	$-nC_3H_7$	H	H
128	H	H	$-nC_4H_9$	H	H
129	H	H	$-CH_2CH_2CH_2CH_2CH_2-$		H
130	H	H	$-(CH_2)_2CH=CH_2$	H	H
131	H	H	$-iC_4H_9$	H	H
132	H	H	$-sC_4H_9$	H	H
133	H	H	$-CH_2CH_2$-Ph	H	H

* Diammonium salt

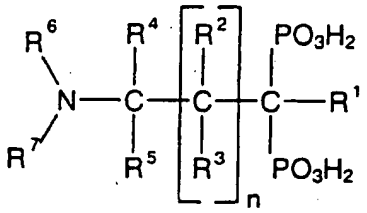


TABLE II

Comp. No.	n	R^1	R^2	R^3	R^4	R^5	R^6	R^7
110*	3	H	H	H	H	H	H	H
111*	3	H	H	H	H	H	H	benzyl
114	2	-OH	H	H	H	H	H	$-CH_3$
115	2	-OH	H	H	H	H	H	$-C_2H_5$
134	3	H	H	H	H	H	H	$-C_2H_5$

* Triammonium salt

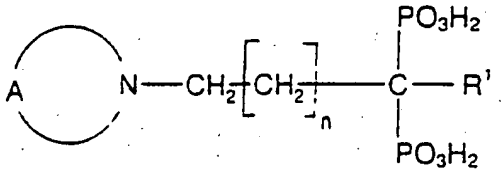
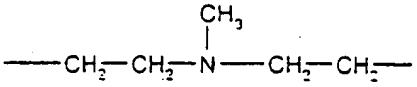


TABLE III

Comp. No.	n	R^1	A
22	1	H	$-CH_2CH_2CH_2CH_2-$
30	1	H	$-CH_2CH_2CH_2CH_2CH_2-$
34	1	-OH	$-CH_2CH_2CH_2CH_2CH_2-$
35	1	-OH	
48	1	-OH	-CH=N-CH=CH-
49	1	-OH	$-CH_2CH_2-O-CH_2CH_2-$
59	1	-OH	$-CH_2CH_2CH_2CH_2-$
77	1	H	$-CH_2CH_2-O-CH_2CH_2-$
116	2	-OH	-CH=N-CH=CH-
135	1	$-NH_2$	$-CH_2CH_2CH_2CH_2CH_2-$

* Tetramethylammonium salt
** Tributylamine salt
*** Trimethylsulfonium salt
**** Diammonium salt

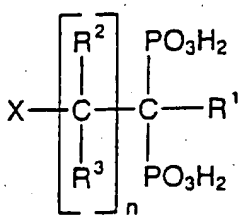


TABLE IV

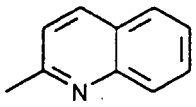
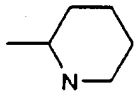
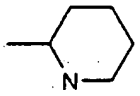
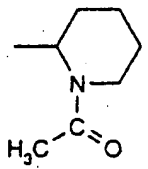
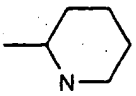
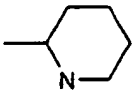
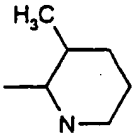
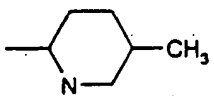
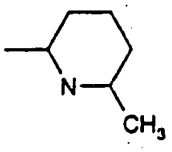
Comp. No.	n	R^1	R^2	R^3	X
1	1	H	H	H	
3	1	H	H	H	
4**	1	H	H	H	
5	1	H	H	H	
6***	1	H	H	H	
8*	1	H	H	H	
9	1	H	H	H	
10	1	H	H	H	
11	1	H	H	H	

TABLE IV

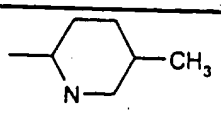
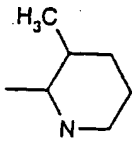
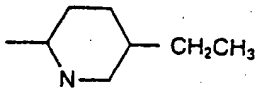
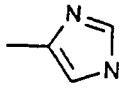
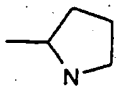
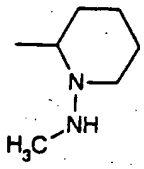
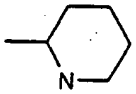
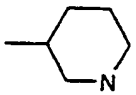
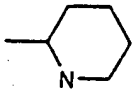
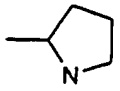
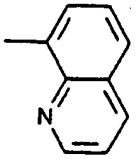
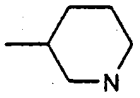
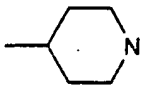
Comp. No.	n	R^1	R^2	R^3	X
12**	1	H	H	H	
13**	1	H	H	H	
16	1	H	H	H	
32	1	-OH	H	H	
33	1	-OH	H	H	
50	1	-OH	H	H	
51	1	-OH	H	H	
67	1	-OH	H	H	
80	1	H	H	$-CH_3$	
107****	1	H	H	H	
112	1	H	H	H	

TABLE IV

Comp. No.	n	R^1	R^2	R^3	X
113	1	H	H	H	
117	1	-OH	H	H	

* Tributylammonium salt
** Tetramethylammonium salt
*** Sodium salt
**** Triammonium salt

HERBICIDAL SCREENING TESTS

The compounds listed in the foregoing tables were tested for herbicidal activity by various methods and at various rates of application. The results of some of these tests are given below. Results obtained in herbicidal screening are affected by a number of factors including: the amount of sunlight, soil type, soil pH, temperature, humidity, depth of planting, plant growth stage, application rate as well as many other factors. All testing procedures are administered with the least amount of variability possible. State of the art equipment and techniques are employed to enable the screening process to remain consistent and reliable.

PRE-EMERGENCE HERBICIDAL SCREENING TEST

On the day preceding treatment, seeds of several different weed species were planted in sandy loam soil containing only trace organic matter. Propagules were sown in individual rows using one species per row across the width of an aluminum flat (19.5 x 9.5 x 6 cm). The grass weeds planted were green foxtail (*Setaria viridis*) ("SETVI"), wild oat (*Avena fatua*) ("AVEFA"), barnyardgrass (*Echinochloa crusgalli*) ("ECHCG"). Broadleaf weeds utilized were wild mustard (*Sinapis arvensis*) ("SINAR"), velvetleaf (*Abutilon theophrasti*) ("ABUTH") and morningglory (*Ipomoea spp.*) ("IPOSS"). Additionally, yellow nutsedge (*Cyperus esculentus*) ("CYPES"), nutlets were sown. Seeding depths ranged from 1.0 to 1.5

cm and plant densities ranged from 3 to 25 plants per row depending on individual plant species.

Solutions of the test compounds were prepared by weighing out 18.8 and 74.7 mg for 1.0 and 4.0 kilograms (acid equivalent) per hectare (kg/ha) applications, respectively, of the test compound into a 60 ml wide-mouth bottle, then dissolving the compound in 14.0 ml of deionized water containing 0.5% v/v Tween 20® (polyoxyethylene sorbitan monolaurate emulsifier) as a surfactant. Additional solvents, not exceeding 2 ml (15% of spray volume), were used if needed to dissolve the compound.

The soil surface was sprayed inside an enclosed linear spray table with the nozzle set at 30.5 cm (12 inches) above the soil line. The spray table was calibrated to deliver 748 L/ha (80 gal/A) with the application rate being 4.0 kg/ha or 1.0 kg/ha. After treatment, the flats were placed into a greenhouse and watered as needed. The greenhouse environmental systems provided the plants with natural and artificial (via metal halide lamps) lighting to attain 14 hours of light per day. Day and night temperatures were maintained at 29° and 21°C, respectively.

The degree of weed control was evaluated and recorded 17-21 days after treatment as a percentage of weed control as compared to the growth of the same species of the same age in an untreated control flat. Percent control is the total injury to the plants due to all factors including: inhibited emergence, stunting, malformation, chlorosis and other types of plant injury. The control ratings range from 0 to 100 percent, where 0% represents no effect with growth equal to the untreated control and where 100% represents complete kill. A dash (--) indicates that no test was performed at that level of application.

POST-EMERGENCE HERBICIDAL EVALUATION

The soil was prepared and seeded with the same species and methodology described for the pre-emergence test. Post-emergence flats were placed in the greenhouse under the same environmental conditions as described for the pre-emergence flats and watered as needed. Plants were grown for 10 to 12 days (or to the appropriate growth stage) prior to compound application. Grasses were sprayed at a 3 to 4 leaf stage and broadleaves at a 1 to 2 leaf stage. Yellow nutsedge was 5 to 7 cm tall at application.

Plants were sprayed 30.5 cm (12 inches) above the foliage with the same spray solution as prepared for the pre-emergence test. The application rate was 4.0 kg/ha or 1.0

kg/ha. Treated plants were then returned to a greenhouse and watered daily without wetting the foliage. The degree of weed control was evaluated 17-21 days after application and recorded as percentage of control as compared to the growth of the same species in an untreated control flat of the same age. The percent control scale (0-100%) used to evaluate the pre-emergence treatment was also applied to the post-emergence treatment, with a dash (--) again indicating that no test was performed at that level of application.

TABLE V - Post-Emergence Testing

Comp. No.	Rate kg/ha	AVEFA	ECHCG	SETVI	ABUTH	IPOSS	SINAR	CYPES
1	4.0	0	0	0	0	--	0	0
2	4.0	0	5	20	0	--	10	0
3	1.0	90	100	100	100	100	100	20
4	4.0	100	100	100	100	100	100	30
5	4.0	20	5	25	0	15	100	0
6	4.0	100	100	100	100	100	100	50
7	4.0	5	10	95	60	90	100	70
8	1.0	90	100	100	100	100	100	25
9	1.0	100	100	98	60	40	100	15
10	1.0	98	100	95	85	60	100	10
11	1.0	10	5	10	10	0	30	0
12	4.0	70	99	90	75	80	--	20
13	4.0	78	97	98	80	85	--	25
14	1.0	100	95	98	75	40	100	25
15	1.0	90	95	98	50	70	98	20
16	1.0	80	95	95	70	15	90	15
17	1.0	95	95	98	60	15	80	10
18	1.0	10	50	95	0	20	20	10
19	1.0	100	98	100	95	20	40	60
20	1.0	60	60	75	100	10	20	10
21	1.0	98	98	100	100	15	70	15
22	1.0	100	98	95	100	70	100	15
23	1.0	80	90	98	100	75	100	50
24	1.0	60	70	70	30	10	30	10
25	1.0	80	75	95	70	20	60	30
26	1.0	70	90	90	20	20	100	10
27	1.0	85	90	98	40	20	30	40
28	1.0	70	80	90	10	25	100	50
29	1.0	100	95	98	95	85	100	40

TABLE V - Post-Emergence Testing

Comp. No.	Rate kg/ha	AVEFA	ECHCG	SETVI	ABUTH	IPOSS	SINAR	CYPES
30	1.0	80	85	90	25	15	95	5
31	4.0	10	60	60	10	0	25	5
32	4.0	15	20	90	30	30	100	5
33	4.0	100	100	100	100	75	100	15
34	4.0	5	20	60	0	30	90	0
35	4.0	0	0	0	0	0	0	0
36	4.0	20	50	40	25	0	15	15
37	4.0	15	15	90	40	20	100	0
38	4.0	0	5	5	0	0	15	0
39	4.0	0	0	15	0	5	15	0
40	4.0	5	0	10	0	5	15	0
41	4.0	85	85	90	25	20	90	10
42	4.0	30	50	98	25	5	100	0
43	4.0	25	50	85	30	30	100	15
44	4.0	0	5	90	10	5	30	5
45	4.0	90	98	98	85	80	100	10
46	4.0	90	95	100	100	60	100	20
47	4.0	90	100	85	20	20	100	5
48	4.0	0	5	20	0	0	20	0
49	4.0	0	0	10	0	0	0	0
50	4.0	5	20	90	80	10	95	5
51	4.0	80	100	95	100	75	100	25
52	4.0	0	20	40	0	5	50	0
53	4.0	0	20	10	15	5	15	0
54	4.0	5	0	5	5	10	85	5
55	4.0	5	30	20	0	5	15	0
56	4.0	70	95	90	80	85	100	60
57	4.0	75	90	95	95	50	100	15
58	4.0	60	95	98	95	50	100	5
59	4.0	30	70	95	70	15	100	15

TABLE V - Post-Emergence Testing

Comp. No.	Rate kg/ha	AVEFA	ECHCG	SETVI	ABUTH	IPOSS	SINAR	CYPES
60	4.0	50	98	90	85	70	100	80
61	4.0	20	98	95	90	20	100	80
62	4.0	10	10	30	60	30	80	50
63	4.0	98	98	20	50	50	100	5
64	4.0	10	10	50	0	5	100	10
65	4.0	5	5	10	10	10	70	10
66	4.0	5	5	5	10	5	50	10
67	4.0	0	0	0	0	0	10	0
68	4.0	40	98	30	10	20	80	10
69	4.0	80	90	90	70	30	100	5
70	4.0	0	10	5	5	0	40	0
71	4.0	40	40	30	15	20	80	40
72	4.0	95	75	15	100	15	100	10
73	1.0	20	10	5	5	5	15	0
74	1.0	80	95	75	85	5	95	10
75	1.0	15	15	25	15	10	40	5
76	1.0	60	80	95	5	30	80	25
77	1.0	5	15	60	20	0	30	0
78	1.0	90	100	98	95	90	100	85
79	1.0	70	85	85	5	5	50	20
80	1.0	40	15	30	0	5	10	0
81	1.0	90	85	60	10	5	85	35
82	1.0	95	95	95	40	10	100	50
83	1.0	95	100	95	65	40	100	40
84	1.0	60	95	90	65	65	100	35
85	1.0	75	95	95	25	15	100	35
86	1.0	98	98	100	85	35	100	75
87	1.0	90	98	98	65	50	100	65
88	1.0	85	90	95	25	15	70	30
89	1.0	75	95	95	10	10	95	15

TABLE V - Post-Emergence Testing

Comp. No.	Rate kg/ha	AVEFA	ECHCG	SETVI	ABUTH	IPOSS	SINAR	CYPES
90	1.0	100	98	98	90	10	85	50
91	1.0	98	95	98	60	5	40	30
92	1.0	10	15	50	0	5	60	0
93	1.0	98	95	98	65	65	100	40
94	1.0	85	94	98	60	75	100	30
95	1.0	95	90	98	100	90	100	25
96	1.0	75	60	70	35	20	25	20
97	1.0	70	60	95	70	20	80	15
98	1.0	90	90	98	70	75	100	20
99	1.0	98	98	100	75	15	100	70
100	1.0	70	40	60	25	10	70	20
101	1.0	100	100	98	80	15	100	20
102	1.0	40	70	85	20	5	60	15
103	1.0	90	95	98	70	20	90	10
104	1.0	98	75	95	65	15	20	10
105	1.0	75	40	70	60	10	90	10
106	1.0	98	98	80	60	20	40	20
107	1.0	100	100	100	95	85	100	25
108	1.0	100	100	100	60	15	90	65
109	1.0	100	98	98	75	40	100	20
110	4.0	85	60	98	15	25	100	35
111	4.0	90	35	60	15	5	95	20
112	4.0	0	0	0	0	0	0	0
113	4.0	0	10	70	15	30	100	5
114	4.0	0	0	0	60	15	10	0
115	4.0	0	0	10	5	0	15	0
116	4.0	0	0	10	0	0	0	0
117	4.0	0	0	0	0	0	0	0
118	1.0	100	100	100	90	65	100	60
119	1.0	100	100	100	98	30	100	95

TABLE V - Post-Emergence Testing

Comp. No.	Rate kg/ha	AVEFA	ECHCG	SETVI	ABUTH	IPOSS	SINAR	CYPES
120	1.0	100	100	100	100	65	100	65
121	1.0	75	65	98	0	20	95	15
122	1.0	100	100	100	80	75	100	50
123	1.0	100	98	100	65	60	100	60
125	1.0	15	0	30	0	0	10	0
126	1.0	100	98	100	65	60	100	60
127	1.0	100	100	100	90	80	100	70
128	1.0	90	75	80	50	50	70	10
129	1.0	100	100	100	100	80	100	85
130	1.0	100	100	100	95	75	100	70
131	1.0	100	100	100	100	95	100	80
132	1.0	100	100	100	95	65	100	70
133	4.0	20	20	50	10	0	70	20
134	4.0	0	0	0	0	0	0	0

Each compound listed in Table V was also tested at the stated application rate for pre-emergence weed control as described above. With the exception of the compounds listed in Table VI below, the tested compounds had no effect on the growth of the listed weed species, i.e., had a 0 percent control rating, when applied pre-emergently.

TABLE VI - Pre-Emergence Testing

Comp. No.	Rate kg/ha	AVEFA	ECHCG	SETVI	ABUTH	IPOSS	SINAR	CYPES
12	4.0	--	--	--	--	--	--	--
13	4.0	--	--	--	--	--	--	--
31	4.0	0	0	0	5	--	5	15
46	4.0	0	0	10	15	10	25	0
110	4.0	0	0	0	0	0	20	0
114	4.0	0	0	0	10	0	0	0

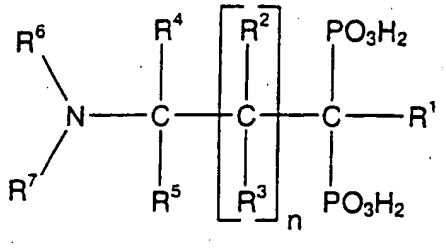
The above data shows the post-emergence efficacy of the herbicidal compounds and compositions of this invention, coupled with their safety to plants when applied pre-emergently.

Although the invention has been described with reference to preferred embodiments and examples thereof, the scope of the present invention is not limited only to those described embodiments. As will be apparent to persons skilled in the art, modifications and adaptations to the above-described invention can be made without departing from the spirit and scope of the invention, which is defined and circumscribed by the appended claims.

WHAT IS CLAIMED IS:

1. An herbicidal composition comprising:

(A) an herbicidally effective amount of a compound of Formula (I)



(I)

wherein

n is 1, 2, 3, 4, 5 or 6;

R^1 is hydrogen, hydroxy, C_1-C_4 alkoxy, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, hydroxy-C_1-C_4-alkyl, hydroxy-C_1-C_4-alkoxy or $N(R^8)(R^9)$ wherein R^8 and R^9 are each independently hydrogen or C_1-C_3 alkyl;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-S(O)m-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{12})(R^{13})$ wherein R^{12} and R^{13} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^6 and R^7 together with the nitrogen to which they are bound form an aziridine; piperazine; morpholine; thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole; tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, halo, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10} alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^6 or R^2 and R^6 together with the nitrogen and carbon atoms to which they are bound form an aziridine; piperazine; morpholine, thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole, tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline; or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^2 and R^4 together with the carbon atoms to which they are bound form a C_5-C_6 cycloalkyl or cycloalkenyl ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10} alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^5 together form a 3-6 membered carbocyclic ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio or $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are each independently hydrogen or C_1-C_{12} alkyl; and

m is 0, 1 or 2;

or an agrochemically acceptable salt or hydrolyzable ester thereof; and

(B) an agrochemically acceptable carrier therefor.

2. A composition according to claim 1, wherein R^1 is hydrogen or hydroxy.

3. A composition according to claim 1, wherein R^2, R^3, R^4 and R^5 are independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl or C_6-C_{10} aralkyl optionally sustituted with halogen or hydroxy.

4. A composition according to claim 1, wherein R^6 and R^7 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl, or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy.

5. A composition according to claim 1, wherein R^4 and R^5 together with the nitrogen and carbon atoms to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1 -C_6 alkyl.

6. A composition according to claim 1, wherein R^6 and R^7 together with the nitrogen to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1 -C_6 alkyl.

7. A composition according to claim 1, wherein n is 1.

8. A composition according to claim 1, wherein

R^1 is hydrogen, hydroxy, halogen or C_1-C_4 alkyl;

R^2, R^3, R^4 and R^5 are independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12} alkyl, halo-C_2-C_{12} alkenyl; halo-C_2-C_{12}-alkynyl; C_6-C_{14} aralkyl; C_1-C_{12} alkoxy; or C_1-C_{12} alkylthio;

R^6 and R^7 are independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12} alkyl; halo-C_2-C_{12} alkenyl; halo-C_2-C_{12} alkynyl; pyridyl; substituted pyridyl; phenyl; substituted phenyl; C_6-C_{14} aralkyl; substituted C_6-C_{14} aralkyl; C_1-C_{12} alkoxy or C_1-C_{12} alkylthio; or

R^2 and R^4 together with the carbon atoms to which they are bound form an optionally substituted C_5-C_6 cycloalkyl or cycloalkenyl ring; or

R^4 and R^6 together with the nitrogen and carbon atoms to which they are bound form a 3- to 7-membered ring optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkylthio or C_7-C_{16} aralkyl; or

R^6 and R^7 together with the nitrogen to which they are bound form a 3- to 7-membered ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy, nitro, C_1-C_6 alkyl, C_7-C_{16} aralkyl or C_1-C_6 alkylthio groups; and

n is 1, 2 or 3.

9. A composition according to claim 1, wherein

R^1 is hydrogen or hydroxy;

R^2 and R^3 are hydrogen;

R^4 and R^5 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; and

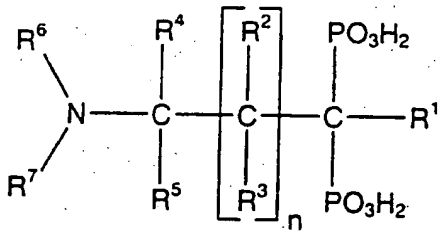
R^6 and R^7 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl, or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; or

R^4 and R^6 together with the nitrogen and carbon atoms to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1-C_6 alkyl; or

R^6 and R^7 together with the nitrogen to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1-C_6 alkyl; and

n is 1.

10. A method of controlling the growth of plants comprising applying to the locus of such plants an herbicidally effective amount of a compound of the Formula (I):



(I)

wherein

n is 1, 2, 3, 4, 5 or 6;

R^1 is hydrogen, hydroxy, C_1-C_4 alkoxy, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, hydroxy-C_1-C_4-alkyl, hydroxy-C_1-C_4-alkoxy or $N(R^8)(R^9)$ wherein R^8 and R^9 are each independently hydrogen or C_1-C_3 alkyl;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{12})(R^{13})$ wherein R^{12} and R^{13} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^6 and R^7 together with the nitrogen to which they are bound form an aziridine; piperazine; morpholine; thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole; tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole;

perhydroquinoline; perhydroisoquinoline or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, halo, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^6 or R^2 and R^6 together with the nitrogen and carbon atoms to which they are bound form an aziridine; piperazine; morpholine, thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole, tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline; or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^2 and R^4 together with the carbon atoms to which they are bound form a C_5-C_6 cycloalkyl or cycloalkenyl ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}- alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^5 together form a 3-6 membered carbocyclic ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio or $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are each independently hydrogen or C_1-C_{12} alkyl; and

m is 0, 1 or 2;

or an agrochemically acceptable salt or hydrolyzable ester thereof.

11. A method according to claim 10, wherein R^1 is hydrogen or hydroxy.

12. A method according to claim 10, wherein R^2, R^3, R^4 and R^5 are independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl or C_6-C_{10} aralkyl optionally sustituted with halogen or hydroxy.

13. A method according to claim 10, wherein R^6 and R^7 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl, or C_6-C_{10} aralkyl oprtionally substituted with halogen or hydroxy.

14. A method according to claim 10, wherein R^4 and R^5 together with the nitrogen and carbon atoms to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1 -C_6 alkyl.

15. A method according to claim 10, wherein R^6 and R^7 together with the nitrogen to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1 -C_6 alkyl.

16. A method according to claim 10, wherein n is 1.

17. A method according to claim 10, wherein

R^1 is hydrogen, hydroxy, halogen or C_1-C_4 alkyl;

R^2, R^3, R^4 and R^5 are independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12} alkyl, halo-C_2-C_{12} alkenyl; halo-C_2-C_{12}-alkynyl: C_6-C_{14} aralkyl; C_1-C_{12} alkoxy; or C_1-C_{12} alkylthio;

R^6 and R^7 are independently hydrogen; C_1-C_{12} alkyl; C_2-C_{12} alkenyl; C_2-C_{12} alkynyl; halo-C_1-C_{12} alkyl; halo-C_2-C_{12} alkenyl; halo-C_2-C_{12} alkynyl; pyridyl; substituted pyridyl; phenyl; substituted phenyl; C_6-C_{14} aralkyl; substituted C_6-C_{14} aralkyl: C_1-C_{12} alkoxy or C_1-C_{12} alkylthio; or

R^2 and R^4 together with the carbon atoms to which they are bound form an optionally substituted C_5-C_6 cycloalkyl or cycloalkenyl ring; or

R^4 and R^6 together with the nitrogen and carbon atoms to which they are bound form a 3- to 7-membered ring optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkylthio or C_7-C_{16} aralkyl; or

R^6 and R^7 together with the nitrogen to which they are bound form a 3- to 7-membered ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy, nitro, C_1-C_6 alkyl, C_7-C_{16} aralkyl or C_1-C_6 alkylthio groups; and

n is 1, 2 or 3.

18. A method according to claim 10, wherein

R^1 is hydrogen or hydroxy;

R^2 and R^3 are hydrogen;

R^4 and R^5 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; and

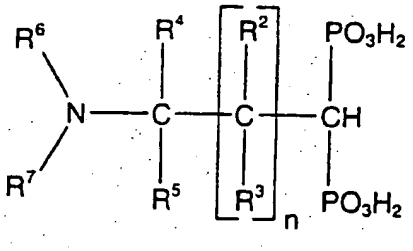
R^6 and R^7 are each independently hydrogen, C_1-C_8 alkyl, C_2-C_8 alkenyl, or C_6-C_{10} aralkyl optionally substituted with halogen or hydroxy; or

R^4 and R^6 together with the nitrogen and carbon atoms to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1-C_6 alkyl; or

R^6 and R^7 together with the nitrogen to which they are bound form a pyrrolidine or piperidine ring, either of which may be optionally substituted with halogen, hydroxy, C_1-C_6 alkoxy or C_1-C_6 alkyl; and

n is 1.

19. A compound having the Formula (II):



(II)

wherein

n is 1, 2, 3, 4, 5 or 6;

each R^2, R^3, R^4 and R^5 is independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; or substituted hydrocarbyl-$S(O)_m$-;

R^6 and R^7 are each independently hydrogen; hydrocarbyl; substituted hydrocarbyl; hydrocarbyloxy; substituted hydrocarbyloxy; hydrocarbyl-$S(O)_m$-; substituted hydrocarbyl-$S(O)_m$-; pyridyl; substituted pyridyl; or are of the formula $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; or

R^6 and R^7 together with the nitrogen to which they are bound form an aziridine; piperazine; morpholine; thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole; tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline or pyrrolidine ring; any of which may be optionally

substituted with C_1-C_{12} alkyl, halo, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10} alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^6 or R^2 and R^6 together with the nitrogen and carbon atoms to which they are bound form an aziridine; piperazine; morpholine, thiomorpholine; thiomorpholine sulfinyl; thiomorpholine sulfonyl; hexamethyleneimine; piperidine, tetrahydropyridine; pyrazole; imidazole; pyrrole; triazole, tetrahydropyrimidine; dihydroimidazole; pyrroline; azetidine; perhydroindole; perhydroquinoline; perhydroisoquinoline; or pyrrolidine ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10}-alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^2 and R^4 together with the carbon atoms to which they are bound form a C_5-C_6 cycloalkyl or cycloalkenyl ring; any of which may be optionally substituted with C_1-C_{12} alkyl, hydroxy, C_1-C_{10} hydroxyalkyl, C_1-C_5 haloalkyl, halo, C_6-C_{10} aryl, C_6-C_{10} aryl substituted with halo or C_1-C_6 alkyl, C_7-C_{16} arylalkyl, C_7-C_{16} arylalkyl substituted with halo or C_1-C_6 alkyl, nitro, halo-C_1-C_{10} alkyl, C_1-C_{10} alkoxy, C_1-C_{10} alkylthio, C_1-C_{10} alkylsulfonyl, phenoxy, phenoxy substituted with halo or C_1-C_6 alkyl, C_2-C_{10} alkenyl or cyano; or

R^4 and R^5 together form a 3-6 membered carbocyclic ring, optionally substituted with halogen, hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio or $N(R^{10})(R^{11})$ wherein R^{10} and R^{11} are each independently hydrogen or C_1-C_{12} alkyl; and

m is 0, 1 or 2;

with the proviso that when n is 1, at least one of R^2, R^3, R^4, R^5, R^6 and R^7 is not H;

or an agrochemically acceptable salt or hydrolyzable ester thereof.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PC1/US 96/04869

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N57/18 C07F9/38 C07F9/40 C07F9/60 C07F9/572
C07F9/59 C07F9/6506 C07F9/6509 C07F9/6533

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 274 158 (NORWICH EATON PHARMACEUTICALS, INC.) 13 July 1988 see page 8, lines 19-21 and page 9, lines 54, 55 ---	1-19
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 July 1996	22.07.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Beslier, L

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	GB,A,1 508 772 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ BV) 26 April 1978 see the whole document	1-18
Y	DD,A,284 155 (KARL-MARX UNIVERSITÄT-LEIPZIG) 7 November 1990 see the whole document	1-18
P,Y	WO,A,95 10188 (ZENECA LTD.) 20 April 1995 see the whole document	1-18
X	WO,A,93 24494 (THE PROCTER & GAMBLE PHARMACEUTICALS, INC.) 9 December 1993 see page 30, example 2.I and page 32, example 5.I	19
X	CHEMICAL ABSTRACTS, vol. 110, no. 11, 13 March 1989 Columbus, Ohio, US; abstract no. 091390, DUSKA F ET AL: "Technetium-99m-aminohexylidenediphosphonate and technetium-99m-pyrophosphate in the scintigraphic diagnosis of experimental myocardial infarction in dogs" XP002008235 see abstract & NUKLEARMEDIZIN (NMIMAX,00295566);88; VOL.27 (5); PP.226-7, CHARLES UNIV.;MED. FAC.; HRADEC KRALOVE; CZECH. (CS),	19
X	EP,A,0 252 504 (BOEHRINGER MANNHEIM GMBH) 13 January 1988 see page 6, line 56 and claim 1	19
X	FR,A,2 354 338 (BENCKISER-KNAPSACK GMBH) 6 January 1978 see claim 1	19
X	WO,A,94 20508 (EISAI CO. LTD.) 15 September 1994 see pages 59-61; 65, 66; 108, 128-194; 223-226	19

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PC., US 96/04869

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		DE-T-	3789436	25-08-94
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		AU-B-	663966	26-10-95
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		CA-A-	2136824	09-12-93
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		CZ-A-	9402967	12-04-95
		CZ-A-	9402968	17-01-96
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		FI-A-	945593	28-11-94
		FI-A-	945599	25-01-95
		HU-A-	71906	28-02-96
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